(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 144 438**
A1

(12) # EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(21) Application number: 84902055.7

(51) Int. Cl.⁴: B 41 M 5/12

(22) Date of filing: 18.05.84

Data of the international application taken as a basis:

(86) International application number:
PCT/JP84/00248

(87) International publication number:
WO84/04728 (06.12.84 84/28)

(30) Priority: 21.05.83 JP 89644/83

(43) Date of publication of application:
19.06.85 Bulletin 85/25

(84) Designated Contracting States:
GB

(71) Applicant: MITSUBISHI PAPER MILLS, LTD.
4-2, Marunouchi 3-chome
Chiyoda-ku Tokyo 100(JP)

(72) Inventor: SENOH, Hideaki Mitsubishi Seishi
Takasago-Ryo
409-1, Sakaemachi Takasagocho Takasago-shi
Hyogo 676(JP)

(72) Inventor: KOSAKA, Takao 2108, Mikage
Toyotomicho Himeji-shi
Hyogo 679-21(JP)

(72) Inventor: KAGOTA, Nobuhiro Mitsubishi Seishi
Sakaemachi
Shataku 622 Go 391-1, Sakaemachi Takasagocho
Takasago-shi Hyogo 676(JP)

(74) Representative: Hansen, Bernd, Dr.rer.nat. et al,
Hoffmann, Eitle & Partner Patentanwälte Arabellastrasse
4
D-8000 München 81(DE)

(54) **PROCESS FOR PRODUCING PRESSURE-SENSITIVE SHEET MATERIAL.**

(57) A process for producing pressure-sensitive sheet material comprising a sheet-form support having a surface coated with pressure-rupturable microcapsules, such as no-carbon required paper, pressure-sensitive adhesive sheet, etc., which process comprises coating a microcapsule-carrying side of a pressure-sensitive material with a coating solution containing defatted soybean powder prepared by treating with an alcohol soybeans defatted according to a solvent extraction process for denaturation. The coating solution containing the defatted soybean powder shows a depressed increase in viscosity of the solution upon its preparation, shows good solution fluidity and good water retention, and undergoes less changes in solution composition. In addition, it reduces unexpected rupture of microcapsules by weak pressure to remarkably decrease color stain on no-carbon required paper, pressure-sensitive paper, etc.

EP 0 144 438 A1

0144438

DESCRIPTION

METHOD OF MAKING PRESSURE SENSITIVE SHEET MATERIALS

TECHNICAL FIELD

This invention relates to a novel method of making pressure sensitive sheet materials. More particularly, it relates to an improvement in the method for making pressure sensitive sheet materials, such as carbonless pressure sensitive recording paper and pressure sensitive adhesive sheet, comprising a support in sheet form and, provided thereon, a coating of pressure-rupturable microcapsules.

BACKGROUND ART

There are known a large variety of pressure sensitive sheet materials. A typical example is a carbonless pressure sensitive recording paper utilizing the color reaction which takes place in a solvent medium between a colorless dye and a color developer such as activated clay, acid clay, phenol resins, aromatic carboxylic acids or metallic salts thereof.

Examples of carbonless pressure sensitive recording sheets include a combination type comprising, on one hand, a sheet carrying a coating formed by emulsifying a solution of a colorless dye dissolved in a solvent, encasing the emulsified finely divided liquid particles

in protective pellicles of natural or synthetic polymers (i.e. microencapsulation), and coating the resulting microcapsule suspension on a support, and, on the other hand, a sheet comprising a support and, provided thereon, a coating of color developers; and a single-layer type comprising a support and, provided thereon, a coating containing both the said microencapsulated colorless dye and the color developer or microencapsulated color developer. There is also known another combination-type carbonless pressure sensitive recording paper comprising a sheet carrying a coating of microencapsulated solution of a color developer and a sheet carrying a coating of a colorless dye.

Other pressure sensitive sheet materials than the carbonless recording paper include a pressure sensitive adhesive sheet carrying a coating of adhesive-containing microcapsules or a coating of solvent-containing microcapsules and an adhesive, and an encapsulated perfume sheet carrying a coating of microencapsulated perfume.

The carbonless pressure sensitive recording sheet materials, which are commercially manufactured on the largest scale of all other pressure sensitive sheet materials, are now in use in various commodity areas such as computer output recording sheets, business slips, and business manifolding forms, and are required to have performance characteristics which comply with the requirements of particular uses. For this reason, in preparing the microcapsule dispersion, various auxiliary

agents are added to meet various requirements. Above all, many proposals have heretofore been made to use, as stilt material, powdered pulp, starch powder, glass beads, plastic beads, talc, calcium carbonate, and clays for the purpose of enhancing the resistance of the microcpasule-coated sheet materials against those unintentional pressing, scuffing, impact, and the like which would cause smudging due to rupture of the microcapsules during manufacture, handling, printing, or actual use of the microcapsule-coated sheet.

Examples of proposed stilt materials for use in carbonless pressure sensitive recording paper include fine powders of starch and starch derivatives (Japanese Patent Publication No. 1,178/72), starch grains having an average diameter as large as at least about 1.2 times the microcapsule diameter (Japanese Patent Publication No. 33,204/73), corncob (waste part of an ear of corn after removal of corn grains) [Japanese Patent Application "Kokai" (Laid-opne) No. 16,708/73], microspheres expandable by heating [Japanese Patent Application "Kokai" (Laid-open) No. 32,013/73], starch grains of large diameter derived from beans other than soybean [Japanese Patent Application "Kokai" (Laid-open) No. 34,013/76], acid-modified polyolefin particles [Japanese Patent Application "Kokai" (Laid-open) No. 111,810/78], water-insoluble vegetable proteins [Japanese Patent Application "Kokai" (Laid-open) No. 58,510/79], finely powdered polyolefin [Japanese Patent Application "Kokai" (Laid-open) No. 51,611/79],

finely powdered polyolefin for use in self-contained pressure sensitive recording paper of the single layer type [Japanese Patent Application "Kokai" (Laid-open) No. 3,969/80], powdered cellulose (US Patent 2,711,375), and finely powdered starch (Brit. P. 1,232,347).

Stilt materials generally used for the purpose of preventing the recording sheet from the smudging due to unintentional rupture of the microcapsules are finely powdered cellulose, finely powdered raw starch, talc, kaolin, bentonite, pyrophyllite, and inorganic pigments such as zinc oxide, titanium oxide, and alumina.

As described above, for the purpose of preventing the carbonless pressure sensitive recording paper from smudging due to unintentional rupture of microcapsules during manufacture, fabrication, printing, or actual use of the recording paper, various proposals have been made and helpful in bringing about a certain degree of improvement. In particular, powdered pulp (finely powdered cellulose) and starch grains are excellent, practical stilt materials and are now in worldwide use. However, the use of powdered pulp as stilt material involves various problems such as a difficulty encountered in coating operation resulting from the increase in viscosity of the coating composition during the coating operation, rendering the uniform distribution of stilt material difficult, resulting in, on one hand, stilt-rich coating areas, where the smudging becomes reduced, while the color developing performance becomes deteriorated and, on

the other hand, stilt-poor coating areas where the smudging becomes so enhanced that sufficient performance characteristics are no more obtained from the practical view point.

Therefore, an object of this invention is to provide a method of making pressure sensitive sheet materials which are lessened in susceptibility to the unintensional rupture of microcapsules and the attendant smudging, to an extent sufficient for practical use, while the color developing function being retained or improved.

Another object of this invention is to provide a method of making pressure sensitive sheet materials, according to which it is possible to retard the viscosity increase in the coating composition during manufacture or application and to minimize the fluctuation in component distribution of the coating composition in order to keep the coating surface from deterioration in quality or to keep the distribution of stilt materials uniform throughout the coating composition.

DISCLOSURE OF THE INVENTION

According to this invention, in making a pressure sensitive sheet material by coating a sheet support with pressure-rupturable microcapsules, a defatted soybean powder obtained by treating and modifying defatted soybean with an alcohol is added to a microcapsule layer-forming composition or a composition which forms a layer contiguous

to the microcapsule layer. When the defatted soybean powder obtained by treating and modifying defatted soybean with an alcohol is used as the stilt material, the coating composition is kept from viscosity increase during its manufacture and retains desirable fluidity so as to improve spreadability of the composition; moreover, owing to sufficient water-retentivity of the alcohol-treated defatted soybean powder, the fluctuation in component distribution is kept low throughout the coating composition so that after application of the composition, there is obtained a coat of uniform surface quality. For instance, in the case of a carbonless pressure sensitive recording paper of color developing quality at normal level, the alcohol-treated defatted soybean powder exhibits distinguished stilt effect so that the unintentional rupture of microcapsules and the attendant smudging under light pressing can be minimized.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention is described in detail in the following.

The defatted soybean in powder form contains proteins, fats, fibrous matters, ash; polysaccharides such as galactan and pentosan; saccharides such as sucrose, stachyose, and raffinose; and vitamins.

In manufacturing the defatted soybean, it is general practice to remove, in the first step, fatty matters from the raw soybean by expression or solvent

extraction. Since the removal of fatty matters by expression is insufficient, it has recently become a common practice to use the solvent extraction which reduces the residual fatty matter content of the defatted soybean down to 1% or below. In the extraction, benzene and n-hexane are generally used as the defatting solvent. The treated soybean is stripped of the solvent by treating with steam at elevated temperatures or by treating under reduced pressure or with a solvent vapor at low temperatures.

The defatted soybean powder used in this invention is obtained from the solvent-extracted soybean by treating with alcohols such as methanol, ethanol, and propyl alcohol. If the defatted soybean produced by expression is used as stilt material, owing to the residual oil which amounts to about 8%, there will occur in the coating layer a phenomenon of cissing which hinders uniform distribution of the stilt material. The defatted soybean powder used in this invention is that obtained from the solvent-extracted soybean by treating and modifying with an alcohol to adjust the protein content to 45 to 55%, the water-soluble nitrogen content being 5 to 15% of the total nitrogen content. Such a defatted soybean powder is an effective stilt material and, in addition, has an advantage of improving the water retentivity of the capsule-containing coating composition on account of the presence of water-soluble constituents. If the water-soluble nitrogen content

exceeds 15% of the total nitrogen, gelation will take place in the coating composition, whereas if the content is below 5%, the water retention becomes insufficient. The principal object of treating and modifying the defatted soybean with an alcohol is deodorizing and decoloring. The resulting defatted soybean powder is a powder material which is nonsticky, easy to handle, and pale amber yellow in color. As a consequence, the coating layer containing such a stilt material is excellent in surface brightness.

A powder material prepared by dissolving raw soybean or defatted soybean in an alkali solution and reprecipitating with an acid is generally a high-purity (e.g. 85%) protein substance and substantially devoid of water-solubility, the water-soluble nitrogen content being 1% of the total nitrogen or less. For this reason, as ascertained by the present inventors, such a soybean powder is unsuitable for actual use, because if it is added to a capsule-containing coating composition, the composition becomes less uniform in component distribution, as compared with the composition prepared according to this invention.

The defatted soybean powder used in this invention is amorphous in particle shape and has an average particle size of from 10 to 60 μm, especially preferred size being 20 to 30 μm which are larger than the capsule size, though not limitative. If necessary, the defatted soybean powder can be used in combination with other known stilt materials such as, for example, finely powdered

cellulose or wheat starch to obtain also a desirable result.

Typical examples of the processes for producing microcapsules used in this invention are physical, coacervation, interfacial polymerization, and in situ polymerization processes.

In the case of carbonless pressure sensitive recording paper, typical examples of colorless dyes enclosed in the capsules include phthalides such as 3,3-bis(4-dimethylaminophenyl)-6-dimethylaminophthalide and 3,3-bis(1,2-dimethylindol-3-yl)-5-dimethylaminophthalide; fluoranes such as 3-diethylamino-6-methyl-7-anilino-fluorane, 3-(N-methylcyclohexylamino)-6-methyl-7-anilino-fluorane, 3-diethylamino-6-methyl-7-chlorofluorane, 3-diethylamino-6-methyl-7-chlorofluorane, and 3-diethylamino-7-dibenzylaminofluorane; thiazine compounds such as benzoyl-leuco methylene blue; lactams such as N-(p-nitrophenyl)-rhodamine B lactam; spiro compounds such as 1,3,3-trimethylindolinospiropyrane; and indolyl red. As for the pellicle materials for microcapsules, there may be mentioned, nonlimitatively, unmodified or partially modified natural polymers such as gelatin, cellulose derivatives, and starch derivatives; and synthetic resins such as urea-formaldehyde resin, melamine-formaldehyde resin, reaction products of isocyanate compounds and hexamethylenediamine, and reaction products of adipic acid dichloride and hexamethylenediamine. However, in view of the reinforcement of capsule wall properties such as

heat resistance, solvent resistance, water resistance, chemical resistance, and impact resistance, microcapsules covered with synthetic resins are preferred.

As oily substances which constitute the internal phase of microcapsules, there may be used solvents of high boiling points which can be at least one selected from natural oils such as petroleum- or mineral-base oils, and animal- or vegetable-base oils or from synthetic oils. Especially preferred are those which dissolve the colorless dyes. As examples, mention may be made of alkylated biphenyls, alkylated terphenyls, alkylated naphthalenes, triarylmethanes, diarylalkanes, phthalic esters, phosphoric esters, sulfonic esters, diaryl ethers, and higher alkylbenzenes, but the invention is not limited thereto.

The pressure sensitive sheet material manufactured according to this invention comprises at least a support, microcapsules, and a defatted soybean powder obtained from the solvent-extracted soybean by treating and modifying with an alcohol. In addition to the microcapsules and the said defatted soybean powder, the present sheet material may contain binders including water-soluble natural binders such as starch and carboxymethylcellulose; and water-soluble synthetic binders such as polyvinyl alcohol, polyvinylpyrrolidone, and polyacrylic acid; and latices such as styrene-butadiene latex, styrene-butadiene-acrylic acid latex, butadiene rubber latex, and neoprene rubber latex. Further, if necessary, there may be added, as lubricant or extender, inorganic pigments such as talc,

titanium dioxide, zinc oxide, calcium carbonate, and activated clay; and organic lubricants such as ethylene-bisstearamide.

The coating composition of this invention can be applied by any of the known techniques such as, for example, air knife coating, blade coating, bill blade coating, roll bar coating, three-applicator-roll coating, and curtain coating. In general, the blade coating is effectively used in applying a high-solid content coating composition. The coating composition of this invention can be efficiently applied also by the blade coating technique, because even at high solids concentration, it is hardly subject to fluctuation in distribution of components and has excellent fluidity.

The defatted soybean powder and the microcapsules should be present on the same side of the support. Therefore, it can be added to the coating composition which is to form the microcapsule layer, or to the coating composition which is to form an under- and/or over-layer to the microcapsule layer.

The composition of solvent-extracted soybean is generally described as follows: about 50% or less of crude protein, 25 to 30% of carbohydrate, 3 to 5% of crude fiber, 5 to 6% of ash, and 1% or less of crude fat. Accordingly, one half is protein substances and another half is non-protein substances. According to this invention, defatted soybean containing a certain amount of water-soluble proteins produces a good result. As examples of

commercial products, mention may be made of "S-Sanmeat" (Ajinomoto Co.) extra grade (7.0% of water, 54.0% of protein, and 0.2% of oil) and first grade (7.5% of water, 49.0% of protein, and 0.2% of oil).

The invention is illustrated below in detail with reference to Example, but the invention is not limited thereto. Hereinafter all parts are by weight.

EXAMPLE (Alcohol-treated defatted soybean powder was used.)

Example of microcapsule preparation:

	Parts
Crystal Violet Lactone	4
Benzoyl Leuco Methylene Blue	1
3-Diethylamino-6-methyl-7-anilinofluorane	0.5
Diarylethane-base organic solvent ("Hi-Sol SAS", Trademark, produced and supplied by Nippon Petroleum Chemical Co.)	100

The above solution of an electron donating leuco dye in the high-boiling solvent was emulsified in 100 parts of a 5-% aqueous solution of a styrene-maleic acid copolymer. An aqueous solution of melamine-formaldehyde prepolymer was prepared by heating a mixture (adjusted to pH 9.5 with sodium hydroxide) of 10 parts of melamine, 25 parts of 37-% formalin, and 20 parts of water. The prepolymer solution was added to the above emulsion and allowed to react with stirring at 75°C for 90 minutes. The reaction mixture was cooled to room temperature

and adjusted to pH 9.5 with sodium hydroxide to obtain a microcapsule dispersion. To 100 parts (dry basis) of the dispersion, was added 35 parts of a defatted soybean poder ("S-Sanmeat" extra grade, a product of Ajinomoto Co.; a soybean powder produced by treating solvent-defatted soybean with an alcohol), 35 parts of talc, 17 parts of polyvinyl alcohol, and 17 parts (dry basis) of a styrene-butadiene latex. The mixture was thoroughly stirred to form a dispersion. The dispersion was coated by means of an air knife coater on a plain paper (40 g/m^2 in basis weight) at a coverage of 5 g/m^2 (dry basis) to obtain an upper sheet for a carbonless pressure sensitive recording paper.

COMPARATIVE EXAMPLE 1 (Wheat starch was used.)

An upper sheet was obtained in the same manner as in Example, except that 35 parts of wheat starch was used in place of the defatted soybean powder treated with an alcohol.

COMPARATIVE EXAMPLE 2 (Finely powdered cellulose was used.)

An upper sheet was obtained in the same manner as in Example, except that 35 parts of finely powdered cellulose was used in place of the defatted soybean powder treated with an alcohol.

COMPARATIVE EXAMPLE 3 (No stilt material was used.)

An upper sheet was obtained in the same manner

as in Example, except that the defatted soybean powder treated with an alcohol was omitted and each 13 parts of polyvinyl alcohol and a styrene-butadiene latex were used as binder for 100 parts of the capsules, the coverage with respect to capsules being the same as in Example.

COMPARATIVE EXAMPLE 4 (Defatted soybean not treated with an alcohol was used.)

An upper sheet was obtained in the same manner as in Example, except that 35 parts of solvent-defatted soybean (50% in protein content) not treated with an alcohol was used in place of the defatted soybean powder treated with an alcohol.

COMPARATIVE EXAMPLE 5 (Water-insoluble soybean protein powder was used.)

An upper sheet was obtained in the same manner as in Example, except that 35 parts of a high-purity soybean protein powder having a water-insoluble protein content of about 85% or above was used in place of the defatted soybean powder treated with an alcohol.

Color developer sheet:

A pressure sensitive recording sheet (Mitsubishi NCR paper CF) carrying a coating of an electron accepting solid acid (oil-soluble novolak-type phenol resin) was used as color developer sheet (under sheet). The upper sheet was placed on the under sheet so as to bring both

coated sides in contact with each other and tested for coloring characteristics and smudge characteristics. The test results were as shown in the table. The test results for smudge characteristics were as shown in the table.

Table

	Coloring intensity (D intensity)		Smudge (reflectance) (%)		Viscosity of coating composition (cps)		Fluctuation of component distribution of coating composition
Example	0.50	○	83.7	○	19.0	○	○
Comp. Example 1	0.46	Δ	89.8	○	13.5	○	X
" " 2	0.50	○	83.5	○	59.0	X	Δ
" " 3	0.52	○	66.8	X	15.0	○	○
" " 4	0.49	○	69.2	X	120.5	X	○
" " 5	0.50	○	83.9	○	15.0	○	X

Note for mark:

○ Excellent for practical use.

Δ Unsatisfactory for practical use.

X Unsuitable for practical use.

In the table, the coloring intensity is the intensity of color measured after one hour of pressure application at 90 kg/cm by means of a calender. The smudge is expressed in terms of reflectance measured 24 hours after rubbing under a load of 450 g/cm^3. All numerical values were corrected for the background condition. Marks, ○ and X, were the results of visual inspection performed at the same time.

As is apparent from the table, a recording paper system comprising a powder material obtained by treating and modifying the solvent-defatted soybean with an alcohol showed especially well-balanced practical characteristics, being excellent in coloring characteristics, less subject to smudging, low in viscosity of the coating composition, and less subject to the fluctuation of component distribution in the coating composition.

POSSIBILITY OF INDUSTRIAL APPLICATION

As described in the foregoing, the method of this invention is suitable for the production of carbonless pressure sensitive recording paper, pressure sensitive adhesive sheet, perfume-containing capsule sheet, and the like. Above all, it is especially suited for the production of pressure sensitive recording paper, because it keeps the recording paper from smudging due to uninternational rupture of the microcapsules.

SCOPE OF CLAIMS

1. In a method of making a pressure sensitive sheet material by coating pressure-rupturable microcapsules on a sheet support the improvement which comprises providing on the side of the support carrying said microcapsules a coating layer containing a defatted soybean powder produced by treating and modifying the solvent-extracted soybean with an alcohol.

2. A method of making a pressure sensitive sheet material according to Claim 1, wherein the defatted soybean powder has a protein content of 45 to 55% and the water-soluble nitrogen content is 5 to 15% of the total nitrogen content.

3. A method of making a pressure sensitive sheet material according to Claim 1, wherein the defatted soybean powder has an average particle size of 10 to 60 μm.

4. A method of making a pressure sensitive sheet material according to Claim 1, wherein the coating composition which provides the coating layer containing a defatted soybean powder is obtained by adding said defatted soybean powder to a microcapsule-containing coating composition.

5. A method of making a pressure sensitive sheet material according to Claim 1, wherein the coating composition which provides the coating layer containing the defatted soybean powder contains no capsule and is coated over and/or under the microcapsule layer.

INTERNATIONAL SEARCH REPORT

0144438

International Application No. PCT/JP84/00248

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.[3] B41M5/12

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	B41M5/12-5/22

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

Jitsuyo Shinan Koho 1960-1983
Kokai Jitsuyo Shinan Koho 1971-1983

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	JP, A, 51-34013 (A. E. Staley Manufacturing Co.) March 23, 1976 (23.03.76) & US, A, 3,996,060	1

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
August 6, 1984 (06.08.84)	August 13, 1984 (13.08.84)
International Searching Authority [1]	**Signature of Authorized Officer [20]**
Japanese Patent Office	

Form PCT/ISA/210 (second sheet) (October 1981)